

Thermodynamics of the incommensurate state in Rb_2WO_4 : on the Lifshitz point in $A'A''BX_4$ compounds

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Abstract

We consider the evolution of the phase transition from the parent hexagonal phase $P6_3/mmc$ to the orthorhombic phase $Pmcn$ that occurs in several compounds of $A'A''BX_4$ family as a function of the hcp lattice parameter c/a . For compounds of K_2SO_4 type with c/a larger than the threshold value 1.26 the direct first-order transition $Pmcn - P6_3/mmc$ is characterized by the large entropy jump $\sim R \ln 2$. For compounds Rb_2WO_4 , K_2MoO_4 , K_2WO_4 with $c/a < 1.26$ this transition occurs via an intermediate incommensurate (Inc) phase. DSC measurements were performed in Rb_2WO_4 to characterize the thermodynamics of the $Pmcn - Inc - P6_3/mmc$ transitions. It was

found that both transitions are again of the first order with entropy jumps $0.2 \cdot R \ln 2$ and $0.3 \cdot R \ln 2$. Therefore, at $c/a \sim 1.26$ the $A'A''BX_4$ compounds reveal an unusual Lifshitz point where three first order transition lines meet. We propose the coupling of crystal elasticity with BX_4 tetrahedra orientation as a possible source of the transitions discontinuity.

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I. INTRODUCTION

The orientational ordering of BX_4 tetrahedra drives a rich sequence of structural phases in ionic $A'A''BX_4$ compounds of K_2SO_4 type. In the present communication we are interested in the nature of the phase transition from the parent high-symmetry phase $P6_3/mmc$ (like α - K_2SO_4) to the orthorhombic phase $Pmcn$ (like β - K_2SO_4) that occurs at high temperatures ($T \sim 600 - 800K$) either directly:

$$Pmcn \xrightarrow{T_c} P6_3/mmc \quad (1)$$

(e.g. in K_2SO_4 , Rb_2SeO_4 , K_2SeO_4) or via an intermediate $1q$ -incommensurate (Inc) phase:

$$Pmcn \xrightarrow{T_l} Inc \xrightarrow{T_i} P6_3/mmc \quad (2)$$

as in molybdates and tungstates Rb_2WO_4 , K_2MoO_4 , K_2WO_4 . The last one has the modulation vector $\mathbf{q}=(0, q_b, 0)$ that can be alternatively directed in two other equivalent directions of the 120° star of the hexagonal Brillouin zone. All the transitions are of the order-disorder type and are characterized by the vertical (up/down) orientations of BX_4 tetrahedra. Other, low temperature transitions in $A'A''BX_4$ compounds that are related with the planar orientation of tetrahedra are beyond our consideration (for details, see Refs. [1–3]).

From the viewpoint of the Landau theory of phase transitions, only the lock-in $Pmcn - Inc$ transition should be of the first order. The $Pmcn - P6_3/mmc$ transition should be of the second order since $Pmcn$ is a subgroup of $P6_3/mmc$ and in the Landau functional neither third order nor Lifshits terms are present. The transition $Inc - P6_3/mmc$ should also be of the second order as a transition to the incommensurate phase of the type II. The recently proposed hcp Ising model [3] correctly describes the high-temperature phase diagram of $A'A''BX_4$ compounds. In this model the $Pmcn - P6_3/mmc$ and $Inc - P6_3/mmc$ transitions are of the second order.

The experimental properties of the $Pmcn - P6_3/mmc$ transitions in various compounds of $A'A''BX_4$ family are collected from Refs. [4–10] in Table I as function of the geometrical

factor c/a of their hcp structure. As was shown in our previous study [3] this is the unique parameter that drives the actual phase sequence: for $c/a > 1.26$ the transition is direct, whereas for $c/a < 1.26$ the sequence (2) takes place.

In disagreement with the theoretical prediction, the direct $Pmcn - P6_3/mmc$ transition is of the first order with a large jump of the molar entropy ($\sim R \ln 2$) [7,9] and of the lattice constants ($\sim 2\%$) [5,6]. The Incommensurate phase in Rb_2WO_4 , K_2MoO_4 , K_2WO_4 was relatively poorly studied because of the high hygroscopic nature of these compounds [10,11]. It is known that the $Inc - P6_3/mmc$ transition reveals a substantial discontinuity of the lattice parameter ($\sim 0.2 - 0.7\%$) [10]. To characterize the thermodynamics of the $Pmcn - Inc - P6_3/mmc$ transition we performed Differential Scanning Calorimetry (DSC) measurements in Rb_2WO_4 that are reported in Sec. II. It was found that both transitions are of the first order with entropy jumps of $0.2R \ln 2$ and $0.3R \ln 2$. The $Inc - P6_3/mmc$ transition is a rare example of incommensurate transition that occurs discontinuously.

At $c/a \sim 1.26$ the critical temperatures T_l , T_i , T_c coincide and the $A'A''BX_4$ compounds seem to reveal a triple Lifshitz point, that was found previously only in few experimental systems (for a review see Ref. [12]). The particular property of this Lifshitz point in $A'A''BX_4$ compounds is that all the incoming transition lines are of the first order. This possibility was theoretically studied in Ref. [13] where the discontinuities were modeled by the negative forth-order terms in the Landau functional. To our knowledge this is also the unique example of Lifshitz point in a system where the modulation vector can be directed in more than one equivalent direction.

The main question raised by these systems is why strong discontinuities at $Pmcn - P6_3/mmc$ and $Inc - P6_3/mmc$ transitions appear. Note first that they cannot be ascribed to fluctuation effects that were widely studied last decades in relation with transitions to the modulated phases [14–18]. In such a case the first order character is attributed to the lack of a stable fixed point as in $BaMnF_4$ [19] and the discontinuity is expected to be small due to the smallness of the critical region. We propose that the observed discontinuities are caused by the coupling of the order parameter with elasticity of the crystal that is known [20–22] to

be able to change the order of transition. Introducing in Sec. III the corresponding coupling to the mean-field treatment of the hcp Ising model [3] and comparing the results with the measured jumps of the lattice constant and molar entropy we demonstrate that this coupling can be responsible for the transitions discontinuity.

II. EXPERIMENT

DSC experiments were performed in Rb_2WO_4 crystals to characterize the thermodynamics of the $Pmcn - Inc - P6_3/mmc$ transitions. Due to the very high hygroscopic nature of the material, powder samples were prepared in a special camera in a dry nitrogen atmosphere. DSC experiments have been performed using a Mettler-TA3000 equipment, between room temperature and $820K$. The heating/cooling rate was $5K/min$. DSC thermograms of the investigated sample show the presence of two reversible enthalpic anomalies at about $T_l = 660K$ and $T_i = 746K$, the lock-in and the incommensurate phase transitions, respectively (see Fig. I). The measured molar entropy jumps are $\Delta S_{T_l} = 1.4J/K \cdot mol$ and $\Delta S_{T_i} = 1.8J/K \cdot mol$ (approximately 80% of ΔS_{T_i} are taken from the δ -peak of DSC anomaly at T_i and other 20% from the residual specific heat decrease in the temperature interval of about $8K$ below T_i , see Fig. I). These values are given in the Table I in units of $R \ln 2$. An hysteresis of $12.5K$ was observed for the $Pmcn - Inc$ transition, ($T_l = 664 \pm 0.5K$ for heating and $651.5 \pm 0.5K$ for cooling). In contrast, the $Inc - P6_3/mmc$ transition reveals no hysteresis within the error bar of $\pm 0.5K$. This is consistent with extremely small hysteresis of $1K$ observed for $Pmcn - P6_3/mmc$ transition in K_2SO_4 [8].

III. DISCUSSION

The high-temperature order-disorder transitions in $A'A''BX_4$ compounds are described by the in-site averages of the vertical orientation of BX_4 tetrahedra, $\sigma_i = \langle S_i \rangle$ where the pseudo-spin S_i is equal to ± 1 for the up/down tetrahedra orientations [3]. The variables σ_i are equal to zero in the disordered high-temperature phase $P6_3/mmc$. In the low-

temperature phase $Pm\bar{c}n$, they take the equal amplitudes $\sigma_i = \pm\sigma$ and alternate according to $Pm\bar{c}n$ symmetry. In the incommensurate phase a modulation $\sigma_i = \sigma_q(e^{i\mathbf{q}\mathbf{r}_i} + e^{-i\mathbf{q}\mathbf{r}_i}) = 2\sigma_q \cos \mathbf{q}\mathbf{r}_i$ occurs. The absolute values of σ_i , and hence of amplitudes σ and $2\sigma_q$ (that define the corresponding order parameters), are smaller than one; the less they are, the more BX_4 tetrahedra are disordered. Because of the discontinuity of the $Pm\bar{c}n - P6_3/mmc$ and $Inc - P6_3/mmc$ transitions the amplitudes σ and $2\sigma_q$ have nonvanishing values below the critical temperatures T_c and T_i . We estimate σ and $2\sigma_q$ in the ordered states from the entropy jump at the transition:

$$\frac{\Delta S}{R} = < \frac{1}{2}((1 + \sigma_i) \ln(1 + \sigma_i) + (1 - \sigma_i) \ln(1 - \sigma_i)) >_i \quad (3)$$

that is measured experimentally (see Table I). For K_2SeO_4 and K_2SO_4 , the inequality $\Delta S > R \ln 2$ holds, which means that in the low temperature phase the BX_4 tetrahedra are perfectly ordered ($\sigma \sim 1$) and, possibly, other degrees of freedom are involved in the transition. Taking σ_i in the incommensurate phase of Rb_2WO_4 as $2\sigma_q \cos \mathbf{q}\mathbf{r}_i$, from $\Delta S = 0.3R \ln 2$ we get $2\sigma_q \sim 0.8$ that again demonstrates the high degree of tetrahedra ordering.

In the mean-field approach of the hcp Ising model [3], the phase transitions from $P6_3/mmc$ to $Pm\bar{c}n$ and to Inc phases were found to be continuous and the free energy (per molecule) was expanded over the small values of parameters σ and $2\sigma_q$ as:

$$f_{com} = \frac{k}{2}(T - T_c)\sigma^2 + \frac{kT}{12}\sigma^4 \quad (4)$$

for $Pm\bar{c}n - P6_3/mmc$ transition, and as:

$$f_{inc} = \frac{k}{4}(T - T_i)(2\sigma_q)^2 + \frac{kT}{32}(2\sigma_q)^4 \quad (5)$$

for $Inc - P6_3/mmc$ transition.

The critical temperatures T_c , T_i are functions of interaction parameters J_{ij} . They coincide at the Lifshitz point and are correlated with the geometrical factor c/a as follows: $T_c < T_i$ when $a/c < 1.26$ and $T_c > T_i$ when $a/c > 1.26$.

To account for the discontinuity of the transitions we propose that coupling of tetrahedra orientation with crystal elasticity is responsible for this phenomenon. Our further consideration is analogous to compressible Ising model, proposed by Domb [20]. For estimation purpose we consider here only the coupling with the strain e_3 along the hexagonal axis and omit other elastic degrees of freedom. Account of those is difficult because of the absence of experimental data, but it can only improve our estimations.

The elastic contribution to the free energy is written as:

$$f_{el} = \gamma\sigma^2 e_3 + \frac{1}{2}V_{mol}C_{33}e_3^2 \quad (6)$$

where $\gamma\sigma^2 e_3$ is the coupling of the order parameter with elastic strain and $V_{mol}C_{33}e_3^2$ is the proper elastic energy of the crystal (per unit volume V_{mol} of the molecule). After minimization we get the strain in the $Pm\bar{c}n$ phase: $e_3 = \Delta c/c = -\gamma\sigma^2/V_{mol}C_{33}$. Substituting it back to (6) we find that coupling with elastic strain renormalizes the quartic term in (4) and the total free energy is written as:

$$f_{com} + f_{el} = \frac{k}{2}(T - T_c)\sigma^2 + (kT/12 - \gamma^2/2C_{33}V_{mol})\sigma^4 \quad (7)$$

The quartic term becomes negative when the elastic contribution $\gamma^2/2C_{33}V_{mol}$ exceeds the Ising thermal energy $kT/12$. The transition then is of the first order and the amplitude of $Pm\bar{c}n$ order parameter is stabilized by the higher order terms.

We estimate the value of the coupling constant γ from the relation $\gamma = -\Delta c/c \cdot V_{mol}C_{33}/\sigma^2$ that, in K_2SO_4 with $C_{33} = 55 \cdot 10^9 N/m^2$ [23], $\sigma^2 \sim 1$, $V_{mol} \sim 120 \text{\AA}^3$ [5] and $\Delta c/c = 0.025$ gives $\gamma \sim -1.7 \cdot 10^{-19} J$. Then, the elastic contribution $\gamma^2/2C_{33}V_{mol} \sim 2.1 \cdot 10^{-21} J$ is indeed larger than $kT_c/12 = 10^{-21} J$ that justifies the role of the elastic degrees of freedom in the discontinuity of $Pm\bar{c}n - P6_3/mmc$ transition.

Consider now the $Inc - P6_3/mmc$ transition. Assuming that the elastic coupling is given by $\gamma < \sigma_i^2 > e_3 = \frac{1}{2}\gamma(2\sigma_q)^2 e_3$, we come to the effective functional

$$f_{inc} + f_{el} = \frac{k}{4}(T - T_i)(2\sigma_q)^2 \quad (8)$$

$$+(kT/32 - \gamma^2/8C_{33}V_{mol})(2\sigma_q)^4$$

We perform the estimation of the quartic coefficient for Rb_2WO_4 in an analogous way as the precedent, taking $2\sigma_q \sim 0.8$ and $V_{mol} \sim 142\text{\AA}^3$ [10]. Since the elastic constant C_{33} is not available we assume it has the same value as in K_2SO_4 . The jump of the lattice parameter $\Delta c/c$ is assumed to be of the same order of 0.007 as in K_2MoO_4 . The calculation gives: $\gamma = -2\Delta c/c \cdot V_{mol}C_{33}/(2\sigma_q)^2 \sim -2 \cdot 10^{-19} J$ and $\gamma^2/8C_{33}V_{mol} \sim 13 \cdot 10^{-22} J$ that again is larger than the bare forth-order coefficient $kT_i/32 = 3 \cdot 10^{-22} J$.

To conclude, we suggest that the Lifshitz point occurs in $A'A''BX_4$ compounds at $c/a \sim 1.26$ where three first-order transition lines meet together. One can expect to achieve this point experimentally, either by preparation of solid solution $Rb_2W_xMo_{1-x}O_4$ or by submitting K_2SeO_4 or Tl_2SeO_4 (with $c/a = 1.27$ and 1.26) to an uniaxial pressure along c . Analyzing experimental data we demonstrate that the coupling of the order parameter with crystal elasticity can be responsible for the discontinuity of transition.

We stress another peculiar feature of the $Pmcn-P6_3/mmc$ and $Inc-P6_3/mmc$ transitions. Despite of the strong entropy jump ($\sim R \ln 2$), they have a very low hysteresis (less than $1K$) that cannot be explained on the basis of the available models [20,21].

It is interesting to note that the $Pmcn-P6_3/mmc$ transition occurs also in another compound of $A'A''BX_4$ family - $KLiSO_4$ that has a large ratio $c/a = 1.69$. Unlike other cases, this transition is either of the second or of the weak first order with the entropy jump less than $0.1R \ln 2$ [24] and with no visible jump of the lattice constants [25]. Then, it is quite probable, that the order of transition changes from the first to the second one and that the $Pmcn-P6_3/mmc$ transition line reveals a tricritical point when c/a increases. More systematic experiments however are needed to verify this hypothesis.

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FIGURES

FIG. 1. DSC thermograms of Rb_2WO_4 in the region of $Pm\bar{c}n \xrightarrow{T_i} Inc \xrightarrow{T_i} P6_3/mmc$ phase transitions on cooling and on heating.

TABLES

TABLE I. The critical temperatures T_l , T_i for $Pmcn$ - Inc - $P6_3/mmc$ transitions and T_c , for $Pmcn$ - $P6_3/mmc$ transitions, the molar entropy jumps and the lattice parameter jumps as functions of lattice parameter c/a . The entropy jumps in Rb_2WO_4 were measured in the present study.

	c/a	T_l, K	T_i, K	$(\frac{\Delta S}{R \ln 2})_{Tl}$	$(\frac{\Delta S}{R \ln 2})_{Ti}$	$(\frac{\Delta c}{c})_{Tl}$	$(\frac{\Delta c}{c})_{Ti}$
		T_c, K		$(\frac{\Delta S}{R \ln 2})_{Tc}$		$(\frac{\Delta c}{c})_{Tc}$	
K_2WO_4	1.24	643	707			$< 0.2\%$	0.2%
K_2MoO_4	1.24	593	733			$< 0.2\%$	0.7%
Rb_2WO_4	1.25	660	746	0.2	0.3		
Tl_2SeO_4	1.26	660					
K_2SeO_4	1.27	745		1.3			
Rb_2MoO_4	1.27	775					
Rb_2SeO_4	1.29	825					
Cs_2SeO_4	1.29	860					
K_2SO_4	1.29	860		2.1		2.5%	
Tl_2SO_4	1.30	773				$< 1.3\%$	

